Effect of pH on separating ions from brackish water using nanofiltration membrane

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Abstract

The effect of pH on the rejection of ions was studied. Two different salts were used at three different pH values. The used salts were NaCl and Na_2SO_4, and the used pH values were 3, 7 and 10. The membrane zeta potential was measured by using NaCl at two different concentrations which are 0.01M and 0.1M. Then the pH of each solution was changed to different values ranging between 3 and 10.

Keyword: Nanofiltration, pH, zeta-potential.

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1. Introduction

Nanofiltration membrane is a new method that is been used widely such as in water treatment, dairy production, removing organic materials, removing heavy metals, removing viruses and bacteria, and concentrating organic dyes. Nanofiltration membrane has properties lying between ultrafiltration membrane and reverse osmosis membrane properties. In order to try to understand nanofiltration membrane separating mechanisms lots of work should be done. These studies should be done at different conditions in order to get a clearer vision about the separation mechanisms. For example, different feed materials at different concentrations, different pH values, inlet flow-rate, temperature and TMP. Such conditions are related to each other and cannot be studied separately, so in order to get an idea about each condition effect, one condition should be changed while keeping the others constant.

In this paper the solution pH was the variable parameter, while the concentration was kept constant at 0.1M for each salt, the temperature was at room temperature, TMP changed from 0.15 to 1.9 bar. For each single and mixed solution, a pH value was adjusted at 3, 7 and 10, to study the effect of the solution pH on the rejection of nanofiltration for a single salt and a mixed salts solutions. This would be done to try to understand the effect of pH on the ions rejection along with the existence of different ion types. The zeta potential for both membranes was measured in-order to find the membrane charge and under what conditions it would change because it is a very important parameter that would explain the ions rejection behaviour by ceramic nanofiltration membrane. Such procedure would be followed in-order to try to establish a relation between the ion type, the ion concentration and the pH on the zeta potential. From the measurements of zeta potential, the membrane ISP point and the membrane charge were gained.

2. Zeta potential measurements

Two different procedures were used to measure the membrane zeta potential to find what factors affects the zeta potential. In the first procedure, one salt was used to prepare two solutions with different concentrations. For each solution the pH was changed from 3 to 10 values. This was done in order to study the effect of pH and concentration on the membrane zeta potential. In the second procedure, four salts were used, where three different concentration solutions for each salt were prepared. This was done in order to study the effect of salt type and concentration on the membrane zeta potential. The membrane that was used was a ceramic Nanofiltration membrane (the membrane made of TiO_2, with 7.00 mm I.D, 10 mm O.D and length of 190 mm, with 1.0 nm mean pore diameter, from Inopor Company).

2.1. First set of Experiments

The membrane zeta potential was measured by using sodium chloride (NaCl), where two solutions were prepared using NaCl at two different concentrations; the concentrations that were used are 0.01M and 0.1M. Then the pH of each solution was changed to different values ranging between 3 and 10. The pH of the two solutions was changed using 0.1M HCl and 0.1M NaOH solutions. This was done in order to study the effect of pH and ions concentration on the membrane zeta potential. After preparing the solution, the crushed membrane was added to these solutions. But before adding the membrane powder to the solutions mentioned above, the membrane powder was soaked in 0.1M HCl solution for 24 hours; afterwards, the membrane powder was washed with distilled water until it had a neutral pH value. Then the membrane powder was added to the prepared solutions and was left to settle down and the top layer of the solution was taken to measure its zeta potential. The membrane zeta potential was measured using a zeta-sizer device.

2.2. Results

For 0.01M concentration solution, the zeta potential decreased as the pH increased, where the ISP was at pH 5. See figure 1. While for 0.1M concentration solution, the membrane zeta potential decreased as the pH increased, and the ISP was at pH 4.6. See figure 2. The higher the pH, the more negative the membrane zeta potential was. As the concentration increased, the ISP decreased. In addition, the zeta potential values were higher for 0.01M NaCl solution than 0.1M NaCl solution.

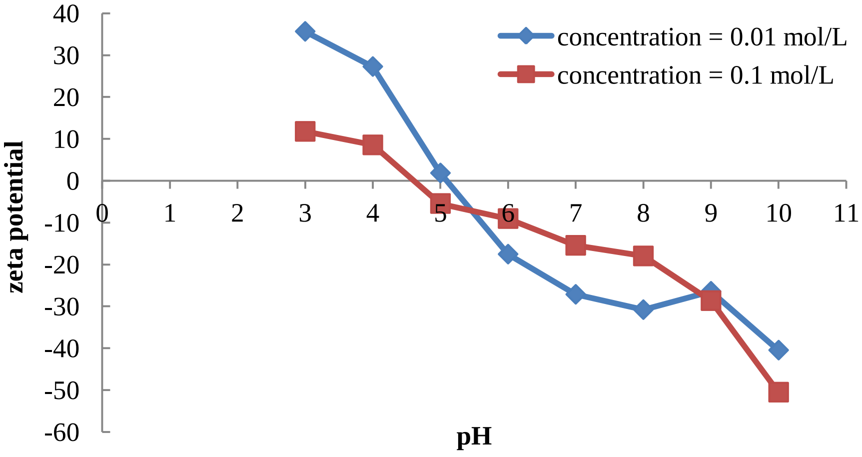

Figure 1. Zeta potential at 0.01M and 0.1M concentration.

2.3. Second set of Experiments

The membrane zeta potential was measured by using four different salts; for each salt three different solutions were prepared at three different concentrations. This was done in order to study the effect of salt type and concentration on the membrane zeta potential. The used salts were sodium chloride (NaCl), magnesium chloride ($MgCl_2$), sodium nitrate ($NaNO_3$) and sodium sulphate (Na_2SO_4). The concentrations that were used are 0.01M, 0.1M and 1.0M. The same procedure that has been described earlier was also used in this part of the experiments.

2.4. Results

The membrane had positive zeta potential values when $MgCl_2$ and NaNO3 solutions were used and negative values when Na_2SO_4 was used. However, when NaCl solution was used, the membrane had a negative zeta potential value for the 0.01M concentration solution, but positive zeta potential values for 0.1M and 1.0M solutions. See figure 2. It was noticed that the membrane zeta potential is affected by salt type and the salt concentration.

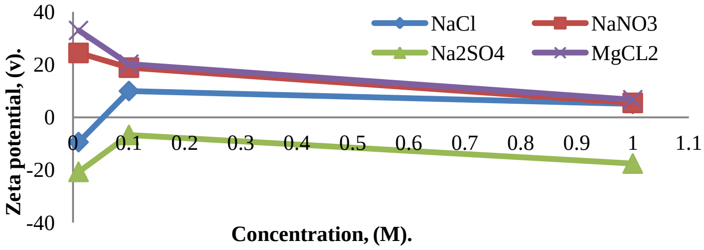

Figure 2. Zeta potential versus concentration for four different salts solutions.

3. pH experiments

The effect of pH on the separation behaviour of nanofiltration membrane was studied for a single and a mixed salts solutions (cation was the common ion). Three different pH values were investigated which were 3, 7 and 10. For each pH value, two single salts and one binary salt solution were prepared and their pH values were adjusted by using 0.1M HCl and 0.1M NaOH solutions.

3.1. Materials

The salts that were used are sodium chloride (NaCl) and sodium sulphate (Na_2SO_4), where the cation Na^{1+} was the common ion. For single and mixed salt solution, a solution with a concentration of 0.1M was prepared at each pH value. The pH was controlled by an acidic solution and a basic solution. The acid solution was 0.1M HCl, which was prepared from 5M HCl laboratory solution. The base solution was 0.1M NaOH, which was prepared by diluting 2 g of NaOH in 500 ml of distilled water. To obtain pH 3, the solution was controlled with 0.1M HCl solution. And to obtain pH 7 and 10, the solutions were controlled with 0.1M NaOH solutions.

3.2. Experimental procedure

At the start of each experiment distilled water was used at first in-order to make sure that the membrane properties did not change. The results of distilled water and brackish water were compared to describe the separation behaviour and to find out if fouling or concentration polarisation took place. At first distilled water was passed through the membrane at constant inlet volumetric flow rate equal to 2.78E-5 m^3/s (100 l/h). The inlet pressure was increased from 0.2 bar to 2.0 bar, which gives a TMP values between 0.15 bar to 1.9 bar. The pressure was increased at 0.5 intervals and run for 30 minute for each TMP value. Permeate of distilled water was collected for 25 minute. The pH and conductivity of distilled water feed and retentate was measured for each TMP value. The same procedure for single and mixed salt solutions was followed but the inlet pressure was increased each 60 minute, where the permeate sample was collected for 55 minute. The pH and the conductivity at each TMP value were measured for the salt solution feed and retentate to make sure that the process was stable and that the feed concentration did not change. After each experiment the membrane was cleaned by 0.1M NaOH solution for 2 hours, and then cleaned by distilled water for at least 18 hours. The ion concentration was measured by ion chromatography and ICP-AES. The ion chromatography measured the anions concentration and ICP-AES measured the cation concentration. Ion chromatography equipment is a Dionex DX600 Ion Chromatograph. The column is a Dionex AS4A-SC. The detector is a conductivity cell and the mobile phase is a mixture of $Na_2CO_3/NaHCO_3$. The ICP-AES samples are diluted and then acidifying them with nitric acid to around $3\%HNO_3$.

3.3. Calculations

The rejection (R) was calculated as follow

$$R = 1 - \frac{C_{i,p}}{C_{i,f}} \qquad (1)$$

where $C_{i,p}$ is the concentration of ion (*i*) in the permeate (mol/m^3) and $C_{i,f}$ is the concentration of ion (*i*) in the feed (mol/m^3). The TMP was calculated as following

$$\mathrm{TMP} = \left(\frac{\mathrm{P_{inlet}}+\mathrm{P_{outlet}}}{2}\right) - \mathrm{P_{permeate}} \qquad (2)$$

Where the pressure at the permeate side was assumed to be equal to zero, and as a result the TMP would be as follows

$$\mathrm{TMP} = \left(\frac{\mathrm{P_{inlet}}+\mathrm{P_{outlet}}}{2}\right) \qquad (3)$$

3.4. Results

The role of pH in separating ions was studied for three different pH values, which were 3, 7 and 10.

3.5.1. Single salt

3.5.1.1. pH 3

The first solution was prepared by diluting NaCl in distelled water, were the concentration was equal to 0.1M. Then the solution pH was changed to reach the value of 3, where the solution pH was adjusted by using 0.1M HCl. For both ions, the highest rejection was at the lowest TMP. When excluding the minimum TMP, the rejection of Cl^{1-} was almost constant and increased a little by increasing the TMP. While for Na^{1+} did not have a constant pattern where it kept increasing and decreasing. But in general, the rejection of Na^{1+} was higher than the rejection of Cl^{1-}, see figure 3. When comparing the permeation of distilled water through the membrane, before and after NaCl solution permeation through the membrane, it was found that distilled water permeation was higher than NaCl solution. This means that fouling did not occur or it was weak and did not have an effect on separation. This is supported by the experimental results where distilled water flux after running the NaCl experiment retained to the same value as before the experiment. See figure 4. NaCl permeate flux (volume flux based on the membrane area) through the membrane increased from 7.7E-07 to 1.6E-05 $m^3/m^2/s$ as the TMP increased.

The rejection of Na^{1+} was higher than the rejection of Cl^{1-}, thus these results cannot be explained by the ion size, because Cl^{1-} has a bigger ion size than Na^{1+} where Cl^{1-} should have a higher rejection than Na^{1+}. However, these results can be explained by the Donnan exclusion, which is the interaction between the membrane and ion charge. In this pH range, the membrane charge is considered to be positive; see section 2.2. Since Cl^{1-} has an opposite charge sign of the membrane charge, attraction would occur causing the Cl^{1-} ion to permeate easily through the membrane, resulting in low rejection. On the other hand, Na^{1+} has the same charge as the membrane charge, which caused repulsion between them, thus the membrane rejected the Na^{1+} ion. The low rejection values for both ions might be due to the electro-neutrality condition and the membrane charge shielding. Due to the electro-neutrality condition, the ions had to move from the higher charge concentration area to the lower charge concentration area until the electro-neutrality condition at both sides of the membrane was reached. As the concentration of ions near the membrane surface starts to build up, as a result a membrane charge shielding by the ions would occur, this would decrease the rejection of Na^{1+} and Cl^{1-} because the Donnan exclusion effect would decrease. The membrane charge shielding effect might be very effective at the highest TMP because Na^{1+} rejection decreased and was lower than Cl^{1-}.

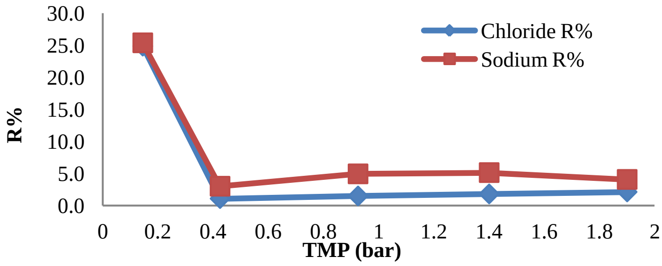

Figure 3. NaCl solution rejection versus TMP at pH = 3.

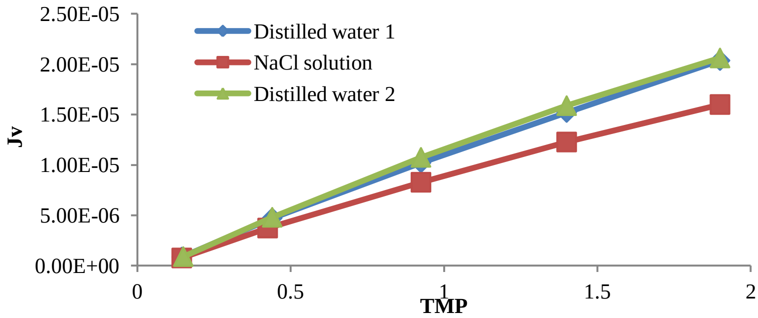

Figure 4. J_v ($m^3/m^2/s$) versus TMP (bar).

The second solution was prepared by diluting Na_2SO_4 in distilled water, where the concentration was equal to 0.1M. The solution pH was controlled by 0.1M HCl solution. The rejection of the cation Na^{1+} was higher than the rejection of anion SO_4^{2-}. The highest rejection of both ions was at the lowest TMP, where the rejection of SO_4^{2-} was about 39.6% and the rejection of Na^{1+} was about 46.5%. When excluding the minimum TMP, the rejection of Na^{1+} was almost constant. While the rejection of SO_4^{2-} did not have a constant pattern where it kept increasing and decreasing. See figure 5. Na_2SO_4 permeate flux through the membrane increased from 2.7E-07 to 5.8E-06 $m^3/m^2/s$ as the TMP increased.

The rejection of Na^{1+} was higher than the rejection of SO_4^{2-}. This cannot be explained by the ion size because SO_4^{2-} has a bigger ion size than Na^{1+}; as a result, SO_4^{2-} should have a higher rejection than Na^{1+}. On the other hand, these results can be explained by Donnan exclusion. Since the membrane charge is considered positive in the pH 3 regions — see section 2.2 — then repulsion between Na^{1+} ion and the membrane charge would occur, moving Na^{1+} away from the membrane and back to the solution. While attraction between the membrane charge and SO_4^{2-} occurs, allowing SO_4^{2-} to permeate through the membrane. As a result, Na^{1+} rejection would increase and SO_4^{2-} rejection would decrease. The low rejection values for both ions can be explained by the electro-neutrality condition and membrane charge shielding. In case of electro-neutrality condition, Na^{1+} and SO_4^{2-} had to permeate from the feed side to the permeate side until the electro-neutrality condition is reached at both sides of the membrane, which caused their rejection to decrease. In the case of membrane charge shielding, the ion concentration at the membrane surface increases then counter-ions would interact with the membrane charge decreasing the membrane ability to reject co-ions, thus decreasing ion rejection.

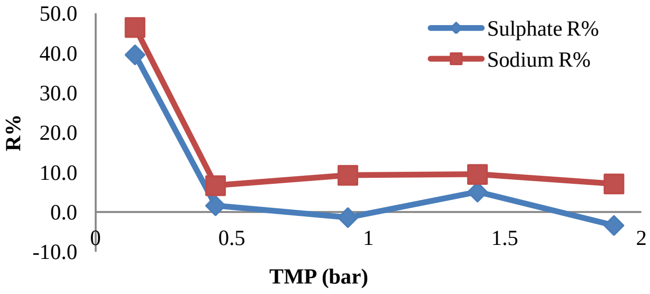

Figure 5. Na_2SO_4 solution rejection versus TMP at pH = 3.

3.5.1.2. pH 7

The first solution was prepared by diluting NaCl in distilled water, where the concentration was about 0.1M. Then the solution pH was adjusted to the value of 7 by using 0.1M NaOH solution. NaCl permeate flux through the membrane increased from 3.0E-07 to 5.6E-06 $m^3/m^2/s$ as the TMP increased. The rejection Cl^{1-} ions was lower than the rejection of Na^{1+} ions and the highest rejection of both ions was at the lowest TMP, where the rejection of Cl^{1-} was about 38.8% and the rejection of Na1+ was about 42.3%. See figure 6. This cannot be explained by the ion size because Cl^{1-} has a bigger ion size than Na^{1+}, thus Cl^{1-} should have a higher rejection. Also, these results cannot be explained by the ion charge, since Cl^{1-} has the same charge sign as that of the membrane — see section 2.2 — where repulsion occurs, causing Cl^{1-} ions to diffuse back to the solution, resulting in higher Cl^{1-} rejection, but Na^{1+} rejection was higher than Cl^{1-} rejection. These results might be due to ion diffusivity through the membrane material. If Cl^{1-} has a higher diffusivity coefficient through the membrane material than Na^{1+}, it would pass more easily through the membrane thus resulting in lower rejection than Na^{1+}. The low rejection values for both ions can be explained by the electro-neutrality condition, where the ions had to move from the higher charge concentration area to the lower charge concentration area until electro-neutrality condition at both sides of the membrane was reached, and as result, their rejection would decrease. As the concentration of Na1+ in the area near the membrane surface area increases, the membrane charge becomes neutralised, which would affect the membrane ability to reject ions. As a result, the ion rejection would decrease because ions can permeate more freely through the membrane.

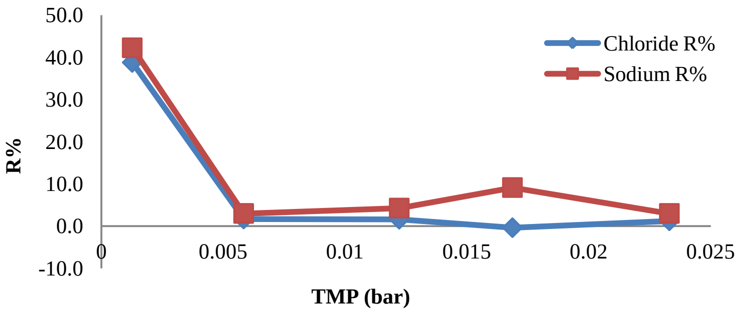

Figure 6. NaCl solution rejection versus TMP at pH = 7.

The second solution was prepared by diluting Na2SO$_4$ in distilled water, where the concentration was about 0.1M. Then the solution pH was adjusted to the value of 7 by using 0.1M NaOH solution. Na2SO4 permeate flux through the membrane increased from 2.5E-07 to 4.5E-06 m^3/m^2/s as the TMP increased. The highest rejection of both ions was at the lowest TMP, where the rejection of SO$_4^{2-}$ was about 55.2% and the rejection of Na^{1+} was about 48.0%. When excluding the lowest TMP value, the rejection of SO$_4^{2-}$ and Na^{1+} remained constant as the TMP increased. See figure 7.

The rejection of Na^{1+} was lower than the rejection of SO$_4^{2-}$. This might be related to the ion size and Donnan exclusion. Where SO$_4^{2-}$ ion has a bigger ion size than Na^{1+} where it would be harder for SO$_4^{2-}$ to permeate through the membrane than Na^{1+}, thus SO$_4^{2-}$ would have a higher rejection. Also, these results can be explained by the ion charge, since SO$_4^{2-}$ has the same charge sign as that of the membrane. Therefore, repulsion occurs, causing the SO$_4^{2-}$ ion to diffuse back to the solution resulting in higher rejection than the rejection of Na^{1+}. If ion speciation was taken into consideration, it would have increased the rejection of SO$_4^{2-}$. Where SO$_4^{2-}$ would react with H^{1+} forming HSO$_4^{1-}$, and since it has the same charge as the membrane, the membrane would reject HSO$_4^{1-}$ because of the repulsion interaction between them, and since it has a big ion size, its rejection would increase. The low rejection values for both ions can be explained by the electro-neutrality condition, were Na^{1+} and SO$_4^{2-}$ had to move from the higher charge concentration area to the lower charge concentration area. Low rejection might also be caused by the increase in Na^{1+} concentration near the membrane surface, where the membrane charge becomes neutralised, which would affect the membrane ability to reject ions. As a result, the ion rejection would decrease because it can permeate more freely through the membrane.

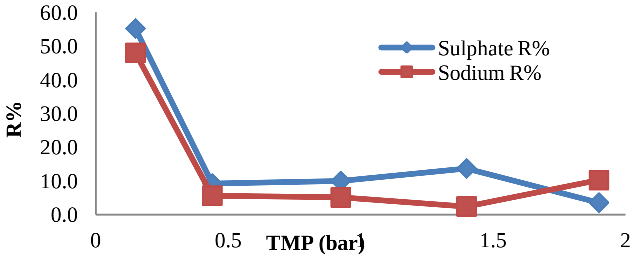

Figure 7. Na$_2$SO$_4$ solution rejection versus TMP at pH = 7.

3.5.1.3. pH 10

The first solution was prepared by diluting NaCl in distilled water, where the concentration was about 0.1M. Then the solution pH was adjusted to the value of 10 by using 0.1M NaOH solution. NaCl permeate flux through the membrane increased from 4.19E-07 to 8.67E-06 $m^3/m^2/s$ as the TMP increased. The highest rejection of both ions was at the lowest TMP, where the rejection of Cl^{1-} was about 27.5% and the rejection of Na^{1+} was about 25.5%. When excluding the lowest TMP value, the rejection of Cl^{1-} increased as the TMP increased. On the other hand, the rejection of Na^{1+} decreased as the TMP increased until it reached 0.925 bar, then it started to increase as the TMP increased. See figure 8.

The rejection of Na^{1+} was lower than the rejection of Cl^{1-}. This can be explained by the ion size, since Cl^{1-} has a bigger ion size than Na^{1+}, thus Cl^{1-} permeating through the membrane pores would be more difficult causing a higher rejection. Also, these results can be explained by the ion charge, where Cl^{1-} has the same charge sign as that of the membrane, thus repulsion occurs causing the Cl^{1-} ion to diffuse back to the solution resulting in higher Cl^{1-} rejection. Also, lower rejection might be due to the neutralisation of the membrane charge by Na^{1+}, which would affect the membrane ability to reject ions. As a result, the ion rejection would decrease because it can permeate more freely through the membrane. The rejection of Na^{1+} and Cl^{1-} might have been affected by the permeation of H^{1+} and OH^{-1} through the membrane. It can be noticed that OH^{-1} ion permeation through the membrane increased as the TMP increased because the permeate pH increased as the TMP increased. In addition, according to the electro-neutrality condition, a specific amount of ions permeates through the membrane, thus the rejection of Cl^{1-} increased. As a result of the increase in the permeation of OH^{1-}, the rejection of Na^{1+} decreased because Na^{1+} had to permeate through the membrane to obtain the electro-neutrality condition. On the other hand, H^{1+} ion should have permeated through the membrane rather than Na^{1+} because it had a smaller ion size. Nevertheless, because of ion speciation, H^{1+} would react with Cl^{1-} forming HCl; as a result, Na^{1+} ions permeated through the membrane to obtain the electro-neutrality condition.

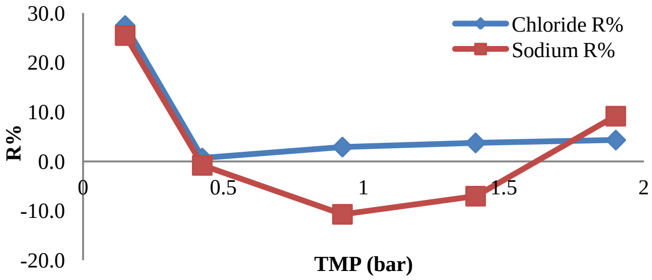

Figure 8. NaCl solution rejection versus TMP at pH = 10.

The second solution was prepared by diluting Na_2SO_4 in distilled water, where the concentration was about 0.1M. Then the solution pH was adjusted to the value of 10 by using 0.1M NaOH solution. Na_2SO_4 permeate flux through the membrane increased from 2.5E-07 to 5.80E-06 $m^3/m^2/s$ as the TMP increased. The highest rejection of both ions was at the lowest TMP, where the rejection of SO_4^{2-} was about 54.6% and the rejection of Na^{1+} was about 48.8%. When excluding the lowest TMP value, the rejection of SO_4^{2-} and Na^{1+} remained constant as the TMP increased. See figure 9.

The rejection of Na^{1+} was lower than the rejection of SO_4^{2-}, which may be due to the ion size and charge. Where the SO_4^{2-} ion has a bigger ion size than Na^{1+}, thus SO_4^{2-} has a higher rejection. Since SO_4^{2-} has the same charge sign as that of the membrane, repulsion occurs, causing the SO_4^{2-} ion to diffuse back to the feeding solution resulting in higher SO_4^{2-} rejection than Na^{1+} rejection. Na^{1+} has an opposite charge of the membrane charge, which caused attraction between Na^{1+} and the membrane charge, resulting in the permeation of Na^{1+} through the membrane.

Low rejection values for both ions can be explained by the electro-neutrality condition and membrane charge neutralisation. Na^{1+} and SO_4^{2-} ions had to move from the higher charge concentration area to the lower charge concentration area until electro-neutrality condition at both sides of the membrane was reached. Additionally, lower rejection might be due to the neutralisation of the membrane charge by Na^{1+}, which would affect the membrane ability to reject ions. As a result, the ions rejection would decrease because they can permeate more freely through the membrane. The rejection of Na^{1+} and SO_4^{2-} might have been affected by the behaviour of H^{1+} and OH^{-1}. Because of ion speciation, H^{1+} would react with SO_4^{2-} forming HSO_4^{1-}; since it has a big ion size and negative charge it would be rejected by the membrane, thus increasing the rejection of SO_4^{2-}. In addition, it can be noticed that OH^{1-} ion permeation through the membrane increased as the TMP increased because the permeate pH increased as the TMP increased. Moreover, according to the electro-neutrality condition, a specific amount of ions permeates through the membrane; consequently, the rejection of SO_4^{2-} increased. Because of the increase in the permeation of OH^{1-} and the decrease in the permeation of H^{1+}, the rejection of Na^{1+} decreased because Na^{1+} had to permeate through the membrane to obtain the electro-neutrality condition.

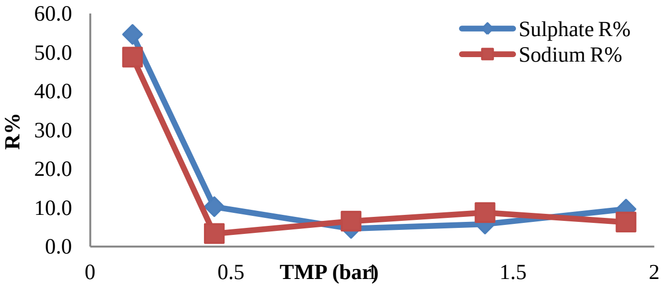

Figure 9. Na_2SO_4 solution rejection versus TMP at pH = 10.

3.5.2. Mixed salt

3.5.2.1. pH3

The solution was prepared by diluting NaCl and Na_2SO_4 in distilled water, where the concentration of each salt was about 0.1M. Then the solution pH was adjusted to the value of 3 by using 0.1M HCl solution. The mixed salt solution permeates flux through the membrane increased from 2.4E-07 to 5.5E-06 $m^3/m^2/s$ as the TMP increased. The highest rejection of all ions was at the lowest TMP, where the rejection of SO_4^{2-} was about 50.0%, the rejection of Cl^{1-} was about 39.0% and the rejection of Na^{1+} was about 49.9%. When excluding the lowest TMP value, the rejection of Na^{1+} remained constant as the TMP increased. On the other hand, the rejection of SO_4^{2-} and Cl^{1-} decreased then increased as the TMP increased. See figure 10.

The rejection of Na^{1+} was higher than Cl^{1-} rejection and was higher than SO_4^{2-} rejection when TMP is lower than 1.4 bar, even though Na^{1+} has the smallest ion size. Na^{1+} rejection is a result of Donnan exclusion, where it has the same charge sign as the membrane charge, which caused repulsion between Na^{1+} and the membrane charge, thus increasing its rejection. While SO_4^{2-} and Cl^{1-} have an opposite charge of the membrane, which caused attraction between them and increased their permeation through the membrane, causing their rejection to decrease. The rejection of SO_4^{2-} was higher than the rejection of Cl^{1-}. This might be due to the ion size, where SO_4^{2-} has a bigger ion size than Cl^{1-}, thus SO_4^{2-} had higher rejection. Furthermore, SO_4^{2-} had a higher rejection than Cl^{1-} due to ion speciation. Where HSO_4^{1-} may have formed, and since it has a bigger ion size than Cl^{1-}, consequently its rejection would be higher.

The low rejection values for all ions might be because of electro-neutrality condition and membrane charge shielding. As the concentration of ions in the area near the membrane surface area increases, the membrane charge becomes neutralised by SO_4^{2-} and Cl^{1-}, which would affect the membrane ability to reject ions. As a result, the ion rejection would decrease because it can permeate more freely through the membrane.

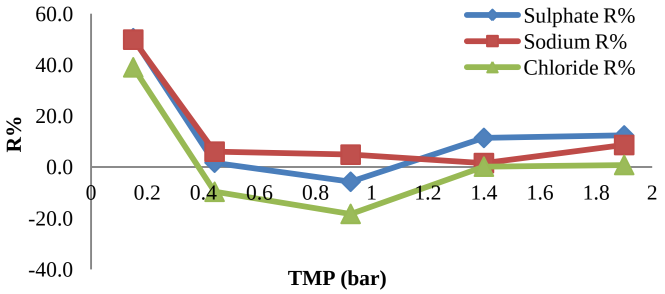

Figure 10. Mixed salts solution rejection versus TMP at pH = 3.

3.5.2.2. pH7

The solution was prepared by diluting NaCl and Na_2SO_4 in distilled water, where the concentration of each salt was about 0.1M. Then the solution pH was adjusted to the value of 7 by using 0.1M NaOH solution. The mixed salt solution permeates flux through the membrane increased from 4.4E-07 to 6.8E-06 $m^3/m^2/s$ as the TMP increased. The highest rejection of all ions was at the lowest TMP, where the rejection of SO_4^{2-} was about 28.4%, the rejection of Cl^{1-} was about 24.1% and the rejection of Na^{1+} was about 32.0%. When excluding the lowest TMP value, the rejection of the three ions remained constant as the TMP increased. It was found that the rejection of Na^{1+} was the highest of them all, then the rejection of SO_4^{2-}, and the lowest rejection was the rejection of Cl^{1-}. See figure 11.

The rejection of SO_4^{2-} was higher than the rejection of Cl^{1-}. This might be due to the ion size, where SO_4^{2-} has a bigger ion size than Cl^{1-} thus SO_4^{2-} had a higher rejection. Also, the SO_4^{2-} ion has a higher ion charge than the Cl^{1-} ion, thus its repulsion away from the membrane would be stronger resulting in higher rejection. Ion speciation may have an effect on the rejection of SO_4^{2-}, where it reacts with H^{1+} forming HSO_4^{1-}. Since it has a negative charge, repulsion between HSO_4^{1-} and the membrane charge (which is negative in this case) forcing HSO_4^{1-} to move away from the membrane and back to the feed solution. Also, HSO_4^{1-} rejection would be higher than Cl^{1-} because it has a bigger ion size. The low rejection values for all ions might be due to the electro-neutrality condition and membrane charge shielding.

In the case of electro-neutrality condition, Na^{1+}, Cl^{1-} and SO_4^{1-} had to move from the higher charge concentration area to the lower charge concentration area until the electro-neutrality condition at both sides of the membrane was reached. Since attraction between the membrane charge and Na^{1+} occurred, the concentration of Na^{1+} near the membrane would start to build up. As a result, the membrane charge would be shielded by Na^{1+} charge and consequently the membrane charge would be neutralised. Because of the membrane charge neutralisation, the permeation of ions through the membrane would be easier; as a result, the rejection of ions by the membrane would decrease.

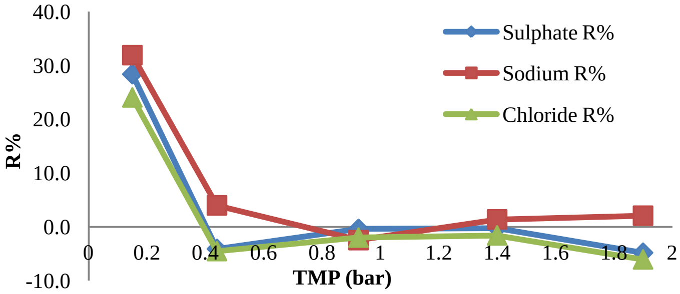

Figure 11. Mixed salts solution rejection versus TMP at pH = 7.

3.5.2.3. pH10

The solution was prepared by diluting NaCl and Na_2SO_4 in distilled water, where the concentration of each salt was about 0.1M. Then the solution pH was adjusted to the value of 10 by using 0.1M NaOH solution. The mixed salt solution permeates flux through the membrane increased from 4.6E-07 to

8.3E-06 $m^3/m^2/s$ as the TMP increased. The highest rejection of all ions was at the lowest TMP, where the rejection of SO_4^{2-} was about 34.1%, the rejection of Cl^{1-} was about 28.8% and the rejection of Na^{1+} was about 38.5%. When excluding the lowest TMP value, the rejection of Na^{1+} ions remained constant as the TMP increased, while the rejections of SO_4^{2-} and Cl^{1-} increased then decreased as the TMP increased. The rejection of Na^{1+} was the highest of them all, and then was the rejection of SO_4^{2-} ions, and the lowest rejection was the rejection of Cl^{1-}. See figure 12. In addition, it can be noticed that OH^{1-} ion permeation through the membrane increased as the TMP increased because the permeate pH increased as the TMP increased.

The rejection of SO_4^{2-} was higher than the rejection of Cl^{1-}, which might be due to the ion size and the ion charge. Since SO_4^{2-} and Cl^{1-} had, the same charge as the membrane, repulsion would occur resulting in rejecting SO_4^{2-} and Cl^{1-} ions to permeate through the membrane. In addition, the SO_4^{2-} ion has a higher ion charge than the Cl^{1-} ion, thus its repulsion away from the membrane would be stronger, resulting in higher rejection. Because of ion speciation, H^{1+} would react with SO_4^{2-} forming HSO_4^{1-}; since it has a big ion size and negative charge, it would be rejected by the membrane, thus increasing the rejection of SO_4^{2-}. This explains the higher rejection of SO_4^{2-} than Cl^{1-} rejection.

The rejection of Na^{1+} was higher than the rejections of Cl^{1-} and SO_4^{2-}, even though Na^{1+} has the smallest ion size and opposite charge sign of that of the membrane charge — see section 2.2 for the membrane charge. According to the electro-neutrality condition, a specific amount of ions permeates through the membrane; consequently, the rejections of Cl^{1-} and SO_4^{2-} increased. As a result of the increase in the permeation of OH^{1-} and the decrease in permeation of H^{1+}, the rejection of Na^{1+} should have decreased because Na^{1+} had to permeate through the membrane to obtain the electro-neutrality condition, but in this case, it increased. The only explanation for Na^{1+} high rejection would be the increase of H^{1+} concentration near the membrane surface. The increase in the concentration of H^{1+} would have shielded the membrane charge, and as a result, repulsion between Na^{1+} and H^{1+} would have occurred, which would increase the rejection of Na^{1+} and decrease the rejections of Cl^{1-} and SO_4^{2-}.

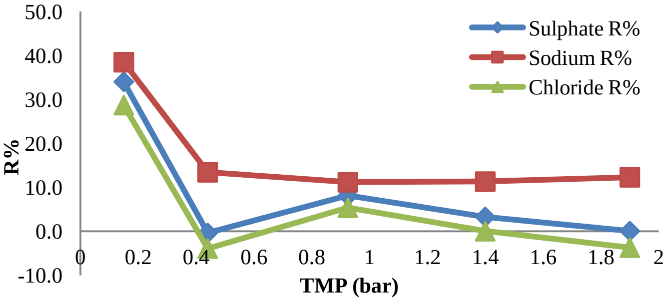

Figure 12. Mixed salts solution rejection versus TMP at pH = 10.

4. Conclusion

Three different pH values were investigated which were 3, 7 and 10. For each pH value, two single salts and one binary salt solution were prepared and their pH values were adjusted using 0.1M HCl and 0.1M NaOH solutions.

- pH 3

For NaCl solution; the rejection of Cl^{1-} ions was lower than the rejection of Na^{1+} ions, and the highest rejection of both ions was at the lowest TMP. For Na_2SO_4 solution; the rejection of SO_4^{2-} ions was lower than the rejection of Na^{1+} ions, and the highest rejection of both ions was at the lowest TMP. For NaCl and Na_2SO_4 solution; the rejection of SO_4^{2-} ions was higher than the rejection of Cl^{1-} ions, and the highest rejection of all ions was at the lowest TMP. The rejection of Na^{1+} was higher than the rejections of Cl^{1-} and SO_4^{2-}, even though Na^{1+} has the smallest ion size. The rejection of Na^{1+} from Na_2SO_4 solution was higher than its rejection from NaCl and mixed salts solution. In addition, the rejection of Na^{1+} from NaCl and mixed salts solutions were similar. At the lowest TMP, the rejections of Na^{1+} from NaCl solution was 25.0%, from Na_2SO_4 solution was 46.0% and from mixed salt solutions was 50.0%. This means the highest rejection of Na^{1+} was from mixed salts solution. The rejection of Cl^{1-} from mixed salt solution (39.0%) was lower than its rejection from NaCl solution (25.0%). As a result, Na^{1+} and Cl^{1-} rejections were dependent on ions type and electrolytes concentrations. On the other hand, the rejection of SO_4^{2-} was independent on ions type and electrolyte concentration.

- pH 7

For NaCl solution; the rejection of Cl^{1-} ions was lower than the rejection of Na^{1+} ions. The highest rejection of both ions was at the lowest TMP. For Na_2SO_4 solution; the rejection of SO_4^{2-} ions was higher than the rejection of Na^{1+} ions. The highest rejection of both ions was at the lowest TMP. For NaCl and Na_2SO_4 solution; the highest rejection of all ions was at the lowest TMP, and if the lowest TMP was excluded then the rejection of the three ions remained constant as the TMP increased. The rejection of Na^{1+} was higher than the rejections of Cl^{1-} and SO_4^{2-}. The rejection of SO_4^{2-} was higher than the rejection of Cl^{1-}.

- pH 10

For NaCl solution; the rejection of Cl^{1-} ions was higher than the rejection of Na^{1+} ions. The highest rejection for both ions was at the lowest TMP. The rejection of Na^{1+} was lower than the rejection of Cl^{1-}. For Na_2SO_4 solution; the rejection of SO_4^{2-} ions was higher than the rejection of Na^{1+} ions. The highest rejection of both ions was at the lowest TMP, but if the lowest TMP was excluded then the rejection of SO_4^{2-} and Na^{1+} remained constant as the TMP increased. For NaCl and Na_2SO_4 solution; the rejection had the following trend: R of Na^{1+} > R of SO_4^{2-} > R of Cl^{1-}. The rejection of Na^{1+} from mixed salts solution was higher than its rejection from single salt solutions. In additions, the rejection of Na^{1+} from Na_2SO_4 solution was higher than its rejection from NaCl solution. The rejection of Cl^{1-} from mixed salts solution was higher than its rejection from NaCl solution. The rejection of SO_4^{2-} from mixed salts solution was lower than its rejection from Na_2SO_4 solution.

In general, the ions rejection was not affected by the change in the pH of the solution. For an example, the rejections of NaCl from a pH controlled solution around pH 3 and 7 and non-controlled pH solutions were similar, but the rejection from a pH 10 solution differed. Where the rejection from pH 10 solution was lower than the rest of the rejection values and the rejection of Cl^{1-} was higher than the rejection of Na^{1+}. Similar results were obtained by P. Puhlfürß et al (ref. 9), where the pH had an effect on the behaviour of the cation and the anion rejection but not the rejections value. The obtained results were compared with G. Hagmeyer and R. Gimbel work (ref. 5), it was noticed that they differed. Where the rejection of NaCl in G. Hagmeyer and R. Gimbel work increased as the permeate flux increased, while in this work the rejection of NaCl decreased as the permeate flux increased. The permeate flux increased as the TMP increased, on the hand the rejection decreased as the TMP increased. This might be due to the difference in the volume flux based on the membrane area values (which is related to the TMP), where the volume flux ranged between 3.0E-7 to 9.0E-6 $m^3/m^2/s$ but in G. Hagmeyer and R. Gimbel work the volume flux ranged between 2.0E-6 to 22.0E-6 $m^3/m^2/s$. The differences between the rejections might be due to the membrane charge, which can be explained through the difference in the zeta potential. In this work, the zeta potential had negative values around pH 5, while in G. Hagmeyer et al. (ref. 5) work the zeta potential had negative values at pH 4. This may increase the negative membrane charge as a result would increase the ions rejection as was noticed in the work of G. Hagmeyer et al. However, in G. Hagmeyer et al. work it was found that the lowest rejection was around the ISP, but this was obtained in this work. This might be due to the difference in the membrane pore radius, where in this work the membrane pore radius was 1.0E-9m but in G. Hagmeyer et al. work, it was 0.7E-9 and 3.32E-9m. Which support the different rejection results obtained by 0.9 and 1.0nm membranes.

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Nomenclature

C_p	is the concentration of ion (i) in the permeate (mol/m^3).
C_f	is the concentration of ion (i) in the feed (mol/m^3).
R	is the rejection.
TMP	is the trans-membrane pressure.

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